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Manganese-Catalyzed Cross-Coupling of Thiols with Aryl Iodides

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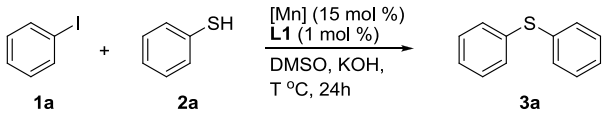
Abstract: Here we report the manganese-catalyzed coupling reaction of thiols with aryl iodides, giving the aryl thioethers in good to excellent yields; the system shows good functional group tolerance and enables the sterically demanding aryl iodides to couple with thiols.

Keywords: manganese • cross-coupling • aryl iodide • dinitrogen ligand • thiol

Introduction

Aryl thioethers are important motifs found in biological chemistry.[1] While many reliable methods have been achieved for preparing such molecules,[1-12] the palladium-catalyzed coupling of thiols with aryl halides and pseudo halides is one of the most popular methods in this transformation.[3] Besides palladium, other catalytic systems using copper,[4] nickel,[5] cobalt,[6] indium,[7] gold,[8] rhodium,[9] iron,[10] and manganese[11] have also been reported for the same purpose. Unfortunately, most of the metals listed above are expensive and toxic; therefore, it is desirable to find an alternative metal for preparation of aryl thioethers. Economically and environmentally benign manganese salts are attractive because manganese is one of the most abundant metals in the world. Although manganese salts have been used for many transformations,[13,14] their use as a catalyst in cross-coupling reactions is relatively unexplored.[15] Recently, Yadavalli et al. reported the manganese-catalyzed coupling reaction between thiols and aryl iodides by using a combination of $MnCl_2$-$4H_2O$ with TMEDA, **L1** as the catalyst, KOH as a base in DMSO at 110 °C for 24 h (Table 1, entry 1).[11] Metal containment-triggered catalysis is a serious issue in recent transition metal catalysis,[16,17] and the presence of trace amounts of transition metals in the base may actually be responsible for cross-coupling.[18] In our hands, using high purity KOH, only poor yield was observed when the reaction was carried out using Yadavalli's conditions (Table 1, entry 2). In addition, even when the reaction temperature was raised to 135 °C, only 29% yield of the desired product was formed (Table 1, entry 3). These results indicated that KOH may contain an impurity which could promote the C-S coupling reaction. In order to clarify the nature of this C-S bond formation using manganese we report the combination of $MnCl_2$ with 1,10-phenanthroline as a reactive catalytic system for the coupling of aryl iodides with thiols. Moreover, the purity of manganese salts has also been extensively examined.

Table 1. Influence of KOH for manganese-catalyzed cross-coupling of iodobenzene with thiophenol.[a]



1a 2a 3a

Entry	[Mn]	Source of KOH	T [°C]	Yield [%]
1	$MnCl_2$-$4H_2O$	KOH	110	82[11]
2	$MnCl_2$ (99.99 %)[b]	KOH (99.99 %)	110	19
3	$MnCl_2$ (99.99 %)[b]	KOH (99.99 %)	135	29

[a] Reaction conditions: Mn source (0.15 mmol, 15 mol %), ligand (0.01 mmol, 1 mol %), iodobenzene (1.2 mmol), thiophenol (1.0 mmol), KOH (1.5 mmol) in 2.0 mL DMSO. [b] Copper, palladium and nickel are not detected by ICP-Mass.

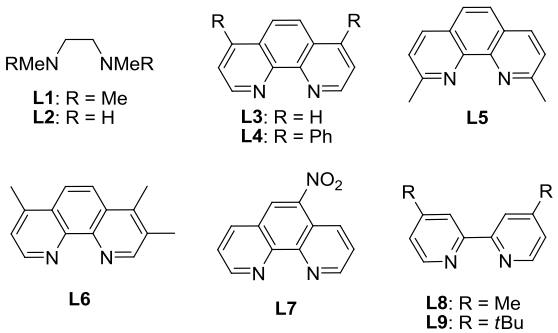


Figure 1. Structures of the ligands **L1-L9.**

Results and Discussion

In order to determine the optimized reaction conditions, 4-iodotoluene and thiophenol were chosen as the model substrates. The results are summarized in Table 2. A series of ligands (Fig. 1) was examined (Table 2, entries 1-9), **L3-L5**, **L8** and **L9** have showed good reactivity for this transformation in dioxane. We then

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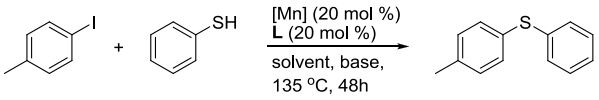
studied the solvent effect (Table 2, entries 10-18) for ligands **L3**-**L5**, **L8** and **L9**. We found toluene to be the most suitable solvent for this reaction; the product was obtained with excellent yields when **L3** and **L4** were used as the ligands (Table 2, entries 10 and 11, respectively). Other solvents such as DMSO, DMF and THF could not provide good results. We also examined the source of base (Table 2, entries 19-23). We found that Cs_2CO_3 is superior to Na_2CO_3, KO*t*Bu, NaO*t*Bu, K_3PO_4 and K_2CO_3. The screening of manganese source (Table 2, entries 24-28) indicated that $MnCl_2$ is still the best salt for the catalysis. Only 35% yield of the product was obtained when the reaction was carried out in the presence of TEMPO (Table 2, entry 29). This result implies the reaction might go through the radical mechanism. A larger scale reaction was also performed by using 10 mmol of thiophenol, giving the product in 99% yield (Table 2, entry 30).

Table 2. Optimize the reaction conditions.[a]



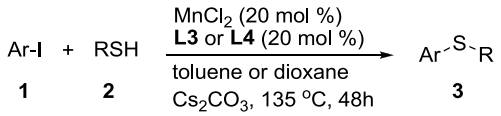
1b **2b** **3b**

Entry	[Mn]	Ligand	Base	Solvent	Yield [%]
1	$MnCl_2$	**L1**	Cs_2CO_3	dioxane	57
2	$MnCl_2$	**L2**	Cs_2CO_3	dioxane	62
3	$MnCl_2$	**L3**	Cs_2CO_3	dioxane	81
4	$MnCl_2$	**L4**	Cs_2CO_3	dioxane	99
5	$MnCl_2$	**L5**	Cs_2CO_3	dioxane	83
6	$MnCl_2$	**L6**	Cs_2CO_3	dioxane	78
7	$MnCl_2$	**L7**	Cs_2CO_3	dioxane	67
8	$MnCl_2$	**L8**	Cs_2CO_3	dioxane	89
9	$MnCl_2$	**L9**	Cs_2CO_3	dioxane	81
10	$MnCl_2$	**L3**	Cs_2CO_3	toluene	99
11	$MnCl_2$	**L4**	Cs_2CO_3	toluene	89
12	$MnCl_2$	**L5**	Cs_2CO_3	toluene	20
13	$MnCl_2$	**L8**	Cs_2CO_3	toluene	5
14	$MnCl_2$	**L9**	Cs_2CO_3	toluene	15
15	$MnCl_2$	**L3**	Cs_2CO_3	DMSO	65
16	$MnCl_2$	**L3**	Cs_2CO_3	DMF	40
17	$MnCl_2$	**L3**	Cs_2CO_3	NMP	22
18	$MnCl_2$	**L3**	Cs_2CO_3	THF	29
19	$MnCl_2$	**L3**	Na_2CO_3	toluene	75
20	$MnCl_2$	**L3**	KO*t*Bu	toluene	59
21	$MnCl_2$	**L3**	NaO*t*Bu	toluene	30
22	$MnCl_2$	**L3**	K_3PO_4	toluene	72
23	$MnCl_2$	**L3**	K_2CO_3	toluene	87
24	$MnBr_2$	**L3**	Cs_2CO_3	toluene	88
25	$Mn(OAc)_2$-$4H_2O$	**L3**	Cs_2CO_3	toluene	76
26	MnO	**L3**	Cs_2CO_3	toluene	30
27	$MnSO_4$-H_2O	**L3**	Cs_2CO_3	toluene	52
28	$MnCl_2$-$4H_2O$	**L3**	Cs_2CO_3	toluene	90
29	$MnCl_2$	**L3**	Cs_2CO_3	toluene	35[b]
30	$MnCl_2$	**L3**	Cs_2CO_3	toluene	99[c]

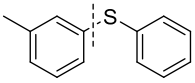
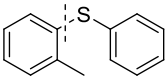
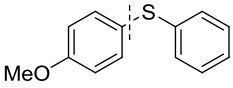
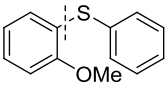
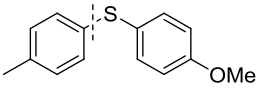
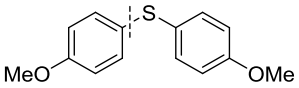
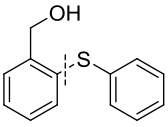
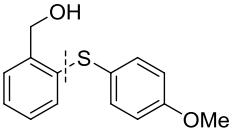
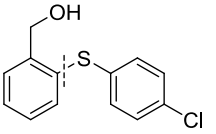
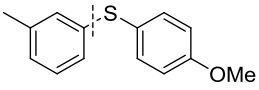
[a] Reaction conditions: Mn source (0.2 mmol, 20 mol %), ligand (0.2 mmol, 20 mol %), 4-iodotoluene (1.2 mmol), thiophenol (1.0 mmol), base (1.5 mmol) in 1.0 mL solvent. [b] 1 equiv of TEMPO was added. [c] 10 mmol scale of thiophenol was conducted.

Based on the optimized reaction conditions, we then studied the scope of this catalytic system. The results are summarized in Table 3, a variety of aryl iodides are coupled smoothly with aryl thiols, giving the corresponding diaryl thioethers in good to excellent yields. Meanwhile, the sterically demanding aryl iodides were also shown to be good coupling partners to provide **3d**, **3f**, **3i**-**3k** (Table 3, entries 2, 4, 7-9). Furthermore, functional groups such as the unprotected alcohol (Table 3, entries 7-9) and chloro (Table 3, entry 9) were both tolerated by the reaction conditions.

Table 3. Manganese-catalyzed S-arylation of aryl iodides with aryl thiols.[a]



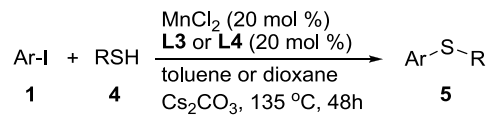
1 **2** **3**

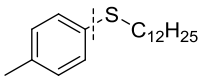
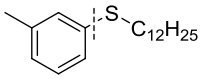
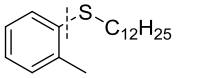
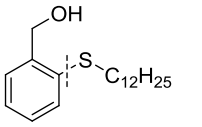
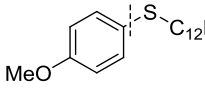
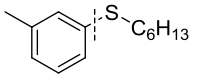
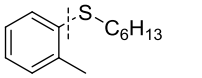
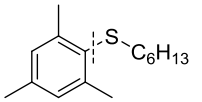
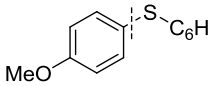
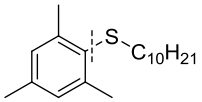
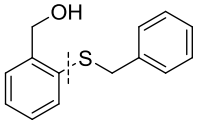
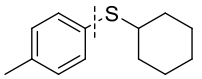
Entry	Product		Yield [%]
1		**3c**	99 98[b]
2		**3d**	91
3		**3e**	99
4		**3f**	80
5		**3g**	99 99[b]
6		**3h**	88
7		**3i**	99
8		**3j**	89
9		**3k**	76
10		**3l**	67[c]

[a] Reaction conditions unless otherwise stated: $MnCl_2$ (0.2 mmol, 20 mol %), **L3** (0.2 mmol, 20 mol %), aryl iodide (1.2 mmol), aryl thiol (1.0 mmol), Cs_2CO_3 (1.5 mmol) in toluene (1.0 mL). [b] 10 mmol scale of thiol was conducted. [c] **L4** (0.2 mmol, 20 mol %) in dioxane (1.0 mL).

We then studied the coupling of aryl iodides with a series of alkyl thiols. The results are listed in Table 4, alkyl thiols including 1-dodecanethiol (Table 4, entries 1-5), 1-hexanethiol (Table 4, entries 6-9), 1-decanethiol (Table 4, entry 10), benzyl mercaptan (Table 4, entry 11) and cyclohexanethiol (Table 4, entry 12) are coupled with a wide spectrum of aryl iodides, affording the aryl alkyl thioethers in moderate to good yields. It is important to note that the aryl iodides bearing the sterically demanding substrates do not reduce the activity of the reactions (Table 4, entries 3, 4, 7, 8, 10 and 11).

Table 4. Manganese-catalyzed S-arylation of aryl iodides with alkyl thiols.[a]



Entry	Product		Yield [%]
1		**5a**	81
2		**5b**	78[b]
3		**5c**	71
4		**5d**	82
5		**5e**	63
6		**5f**	84
7		**5g**	78
8		**5h**	60[b]
9		**5i**	64
10		**5j**	68[b]
11		**5k**	64
12		**5l**	63[b]

[a] Reaction conditions unless otherwise stated: $MnCl_2$ (0.2 mmol, 20 mol %), **L3** (0.2 mmol, 20 mo l%), aryl iodide (1.2 mmol), alkyl thiol (1.0 mmol), Cs_2CO_3 (1.5 mmol) in toluene (1.0 mL). [b] **L4** (0.2 mmol, 20 mol %) in dioxane (1.0 mL).

Conclusion

In conclusion, we have reported the manganese-catalyzed coupling reaction of thiols with aryl iodides. The purity of KOH and metal source has been extensively examined. Functional groups such as unprotected alcohol and chloro are tolerated by the reaction conditions. Moreover, this catalytic system enables the sterically demanding aryl iodides to couple with thiols. A detailed mechanistic study of this catalytic system and applications to other cross-coupling reactions are under progress in our laboratory.

Experimental Section

General information All chemicals were purchased from commercial suppliers and used without further purification. Toluene was dried over sodium; dioxane and DMF were dried over CaH_2 and stored in the presence of activated molecular sieve. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on Merck silica gel 60 (230-400 mesh).

Analysis NMR spectra were recorded on a Varian Unity Inova-600 or a Varian Mercury-400 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, br = broad. Melting points (m.p.) were determined using a Büchi 535 apparatus and are reported uncorrected. GC-MS analyses were performed on a GC-MS analysis on HP 5890 GC equipped with HP 5972 MS. High-resolution mass spectra were carried out on a Jeol JMS-HX 110 spectrometer by the services at the National Chung Hsing University.

General procedure for Table 1 A sealable vial equipped with a magnetic stir bar was charged with $MnCl_2$ (18.6 mg, 0.15 mmol), KOH (84 mg, 1.5 mmol) and TMEDA (1.5 µl, 0.01 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum. Under a nitrogen atmosphere, thiophenol (0.104 mL, 1.0 mmol), iodobenzene (0.138 mL, 1.2 mmol) and DMSO (2.0 mL) were added via syringe. The septum was then replaced by a screw cap containing a PTFE septum, and the reaction vessel was heated at 110 ℃ and 135 ℃ oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was filtered through a pad of celite then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane) to yield the **3a**.

The representative example of Table 1. Diphenyl sulfide **3a** *(Table 1, entry 3)*[3c] Following the general procedure for Table 1, then purified by column chromatography (SiO_2, hexane) to provide the **3a** as a colorless oil (54 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.36 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.0, 129.2, 131.0, 135.7.

General procedure for Table 2 A sealable vial equipped with a magnetic stir bar was charged with $MnCl_2$ (24.8 mg, 0.20 mmol), base (1.5 mmol) and ligand (0.20 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum. Under a nitrogen atmosphere, thiophenol (0.104 mL, 1.0 mmol), 4-iodotoluene (262 mg, 1.2 mmol) and solvent (1.0 mL) were added via syringe. The septum was then replaced by a screw cap containing a PTFE septum, and the reaction vessel was heated at 135 ℃ oil bath. After stirring at this temperature for 48 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was filtered through a pad of celite then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane) to yield **3b**.

The representative example of Table 2. 4-Methylphenyl phenyl sulfide ***3b*** *(Table 2, entry 10)*[3c] Following the general procedure for Table 2, using Cs_2CO_3 (488 mg, 1.5 mmol), **L3** (36.0 mg, 0.2 mmol) and toluene (1.0 mL) to give **3b** as a colorless oil (198 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3 H), 7.09-7.18 (m, 3 H), 7.20-7.29 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 126.3, 129.0, 129.6, 130.0, 131.2, 132.2, 137.1, 137.5.

General procedure for Table 3 A sealable vial equipped with a magnetic stir bar was charged with $MnCl_2$ (24.8mg, 0.2 mmol), Cs_2CO_3 (488 mg, 1.5 mmol), **L3** (36.0 mg, 0.2 mmol) or **L4** (67.2 mg, 0.2 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum, aryl iodide (1.20 mmol), toluene (1.0 mL) or dioxane (1.0 mL) were added via syringe. The arylthiol (1.0 mmol) was then added via syringe, and the vial sealed with a cap containing a PTFE septum and the reaction vessel was heated at 135 ℃ oil bath. After stirring at this temperature for 48 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of celite then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO2, hexane and Ethyl acetate) to yield **3**.

3-Methylphenyl phenyl sulfide ***3c*** *(Table 3, entry 1)*[3c] Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 3-iodotoluene (0.156 mL, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3c** as a colorless oil (198 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (σ, 3 H), 7.04–7.33 (µ, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 126.8, 128.0, 128.3, 129.0, 129.1, 130.7, 131.8, 135.2, 136.0, 139.0.

2-Methylphenyl phenyl sulfide ***3d*** *(Table 3, entry 2)*[3c] Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 2-iodotoluene (0.156 mL, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3d** as a colorless oil (182 mg, 91% yield). ^{1}H NMR (400

MHz, $CDCl_3$): δ 2.37 (s, 3 H), 7.10-7.29 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 126.3, 126.7, 127.9, 129.1, 129.6, 130.5, 132.9, 133.7, 136.1, 139.9.

4-Methoxyphenyl phenyl sulfide ***3e*** *(Table 3, entry 3)*[3c] Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 4-iodoanisole (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3e** as a colorless oil (214 mg, 99% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3 H), 6.85 (dd, *J* = 2.4, 6.8 Hz, 2H), 7.07-7.21 (m, 5H), 7.39 (dd, *J* = 2.0, 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 114.9, 124.1, 125.6, 128.0, 128.8, 135.2, 138.5, 159.7.

2-Methoxyphenyl phenyl sulfide ***3f*** *(Table 3, entry 4)*[3c] Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 2-iodoanisole (0.156 mL, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3f** as a colorless oil (173 mg, 80% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3 H), 6.83-6.90 (m, 2 H), 7.08 (dd, *J* = 1.4, 7.8 Hz, 1 H), 7.19-7.40 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8, 110.8, 121.2, 124.0, 127.0, 128.3, 129.1, 131.4, 131.5, 134.4, 157.2.

4-Methylphenyl 4-methoxyphenyl sulfide ***3g*** *(Table 3, entry 5)*[3c] Following the general procedure for Table 3, using 4-methoxythiophenol (0.126 mL, 1.0 mmol), 4-iodotoluene (262 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3g** as a colorless oil (228 mg, 99% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3 H), 3.74 (s, 3 H), 6.83 (dd, *J* = 2.0, 6.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 7.34 (dd, *J* = 2.4, 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 55.2, 114.7, 125.5, 129.2, 129.7, 134.2, 134.3, 135.9, 159.3.

Di-4-methoxyphenyl sulfide ***3h*** *(Table 3, entry 6)*[3c] Following the general procedure for Table 3, using 4-iodoanisole (287 mg, 1.2 mmol), 4-methoxythiophenol (0.126 mL, 1.0 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3h** as a white solid (217 mg, 88% yield). M.p.: 45-46 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 6 H), 6.80 (d, *J* = 6.8 Hz, 4 H), 7.26 (d, *J* = 6.8 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 114.7, 127.4, 132.7, 158.9.

(2-(Phenylthio)phenyl)methanol ***3i*** *(Table 3, entry 7)*[4d] Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), thiophenol (0.104 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3i** as a colorless oil (214 mg, 99% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.31 (br s, 1 H), 4.74 (s, 2 H), 7.16-7.19 (m, 3 H), 7.21-7.4 (m, 3 H), 7.25-7.36 (m, 2 H), 7.48 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.3, 126.5, 128.4, 128.4, 129.1, 129.4, 132.3, 133.9, 135.9, 142.3.

(2-(4-Methoxyphenylthio)phenyl)methanol ***3j*** *(Table 2, entry 8)*[4g] Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), 4-methoxythiophenol (0.126 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3j** as a colorless oil (219 mg, 89% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.48 (br s, 1 H), 3.78 (s, 3 H), 4.76 (s, 2 H), 6.86 (dt, *J* = 4.0, 9.2 Hz, 2 H), 7.09 (dd, *J* = 1.4, 8.0 Hz, 1 H), 7.13-7.24 (m, 2 H), 7.29 (dt, *J* = 4.0, 8.0 Hz, 2 H), 7.41 (dd, *J* = 1.2, 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 63.3, 115.0, 124.3, 126.8, 128.1, 128.2, 130.4, 134.1, 135.6, 139.8, 159.5.

(2-(4-Chlorophenylthio)phenyl)methanol ***3k*** *(Table 3, entry 9)*[19] Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), 4-chlorothiophenol (145 mg, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **3k** as a colorless oil (190 mg, 76% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.79 (br s, 1 H), 4.70 (s, 2 H), 7.07 (dd, *J* = 4.0, 8.0 Hz, 2 H), 7.17-7.25 (m, 3 H), 7.30-7.33 (m, 2 H), 7.48 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.1, 128.3, 128.4, 128.6, 129.2, 130.5, 131.7, 132.4, 133.8, 134.6, 132.3.

3-Methylphenyl 4-methoxyphenyl sulfide ***3l*** *(Table 3, entry 10)*[3c] Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), 4-methoxythiophenol (0.126 mL, 1.0 mmol), 3-iodotoluene (0.156 mL, 1.2 mmol), **L4** (67.2 mg, 0.2 mmol) in dioxane (1.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **3l** as a colorless oil (154 mg, 67% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.34 (σ, 3 H), 3.75 (σ, 3 H), 6.85 (δδ, ϑ = 2.0, 6.8 Hζ, 2 H), 6.90–6.97 (μ, 2 H), 7.01 (σ, 1 H), 7.09 (τ, ϑ = 7.6 Hζ, 1 H), 7.38 (δδ, ϑ = 2.0, 6.8 Hζ, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 55.2, 114.8, 124.4, 125.4, 126.6, 128.7, 128.8, 135.0, 138.1, 138.6, 159.6.

General procedure for Table 4 A sealable vial equipped with a magnetic stir bar was charged with $MnCl_2$ (24.8 mg, 0.2 mmol), Cs_2CO_3 (488 mg, 1.5 mmol) and **L3** (36.0 mg, 0.2 mmol) or **L4** (67.2 mg, 0.2 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum, aryl iodide (1.20 mmol), toluene (1.0 mL) or dioxane (1.0 mL) were added via syringe. The alkyl thiol (1.0 mmol) was then added via syringe, and the vial sealed with a cap containing a PTFE septum and the reaction vessel was heated at 135 °C oil bath. After stirring at this temperature for 48 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of celite then washed with ethyl acetate (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane and CH_2Cl_2 or Ethyl acetate) to yield **5**.

Dodecyl 4-methylphenyl sulfide ***5a*** *(Table 4, entry 1)*[4a] Following the general procedure for Table 4, 1-dodecanethiol (0.240 mL, 1.0 mmol), 4-iodotoluene (261 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **5a** as a colorless oil (237 mg, 81% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.25-1.31 (m, 16 H), 1.37-1.40 (m, 2 H), 1.56-1.62 (m, 2 H), 2.28 (s, 3 H), 2.84 (t, *J* = 7.4 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.9, 22.6, 28.8, 29.1, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 34.2, 129.5, 129.6, 133.2, 135.5.

Dodecyl 3-methylphenyl sulfide ***5b*** *(Table 4, entry 2)* Following the general procedure for Table 4, 1-dodecanethiol (0.240 mL, 1.0 mmol), 3-iodotoluene (0.156 mL, 1.2 mmol), **L4** (67.2 mg, 0.2 mmol) in dioxane (1.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **3l** as a colorless oil (228 mg, 78% yield).^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 3 H), 1.25-1.30 (m, 16 H), 1.37-1.43 (m, 2 H), 1.59-1.68 (m, 2 H), 2.32 (s, 3 H), 2.90 (t, *J* = 7.4 Hz, 2 H), 6.96 (d, *J* = 6.8 Hz, 1 H), 7.10-7.25 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.3, 22.7, 28.8, 29.1, 29.1, 29.3, 29.5, 29.6, 29.6, 31.9, 33.5, 125.7, 126.4, 128.6, 129.4, 136.7, 138.5. HREI-MS calcd. for $C_{19}H_{32}S$: 292.2225, found: 292.2228.

Dodecyl 2-methylphenyl sulfide ***5c*** *(Table 4, entry 3)*[20] Following the general procedure for Table 4, 1-dodecanethiol (0.240 mL, 1.0 mmol), 2-iodotoluene (0.156 mL, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **5c** as a colorless oil (207 mg, 71% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 6.8 Hz, 3 H), 1.29-1.33 (m, 16 H), 1.43-1.47 (m, 2 H), 1.64-1.72 (m, 2 H), 2.38 (s, 3 H), 2.89 (t, *J* = 7.4 Hz, 2 H), 7.05-7.09 (m, 1 H), 7.13-7.17 (m, 2 H), 7.24-7.27 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.2, 22.7, 29.0, 29.2, 29.3, 29.5, 29.6, 29.6, 29.7, 31.9, 32.7, 32.8, 125.1, 126.2, 127.2, 129.9, 136.4, 137.1.

(2-(Dodecylthio)phenyl)methanol ***5d*** *(Table 4, entry 4)*[4d] Following the general procedure for Table 4, using Cs_2CO_3 (812 mg, 2.5 mmol), 1-dodecanethiol (0.240 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **5d** as a white solid (205 mg, 82% yield): M.p.: 38-39 °C (lit.[4d] 38-39 °C). ^1H NMR (400 MHz, $CDCl_3$): δ0.88 (t, *J* = 7.0 Hz, 3 H), 1.25-1.31 (m, 16 H), 1.38 (m, 2 H), 1.60-1.68 (m, 2 H), 2.37 (br s, 1 H), 2.91 (t, *J* = 7.4 Hz, 2 H), 4.76 (d, *J* = 6.0 Hz, 2 H), 7.18-7.28 (m, 2 H), 7.34-7.38 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 28.8, 29.1, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 33.9, 63.6, 126.1, 128.1, 128.1, 129.2, 135.1, 140.3.

Dodecyl 4-methoxyphenyl sulfide ***5e*** *(Table 4, entry 5)*[4a] Following the general procedure for Table 4, 1-dodecanethiol (0.240 mL, 1.0 mmol), 4-iodoanisole (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **5e** as a colorless solid (194 mg, 63% yield): M.p.: 44-45 °C (lit.[4a] 44-45 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 3 H), 1.30-1.39 (m, 18 H), 1.53-1.62 (m, 2 H), 2.80 (t, *J* = 7.4 Hz, 2 H), 3.78 (s, 3 H), 6.81-6.84 (m, 2 H), 7.31-7.34 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.1, 22.7, 28.7, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 35.8, 55.2, 114.4, 126.9, 132.8, 158.6.

Hexyl 3-methylphenyl sulfide ***5f*** *(Table 4, entry 6)* Following the general procedure for Table 4, 1-hexanethiol (0.141 mL, 1.0 mmol), 3-iodotoluene (0.156 ml, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **5f** as a colorless oil (175 mg, 84% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.85-0.89 (m, 3 H), 1.27-1.33 (m, 4 H), 1.37-1.44 (m, 2 H), 1.58-1.66 (m, 2 H), 2.29 (s, 3 H), 2.86-2.91 (m, 2 H), 6.92-6.95 (m, 1 H), 7.08-7.16 (m, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.0, 21.2, 22.5, 28.5, 29.0, 31.3, 33.4, 125.6, 126.4, 128.5, 129.3, 136.7, 138.4. HREI-MS calcd. for $C_{13}H_{20}S$: 208.1285, found: 208.1279.

Hexyl 2-methylphenyl sulfide ***5g*** *(Table 4, entry 7)* Following the general procedure for Table 4, 1-hexanethiol (0.141 mL, 1.0 mmol), 2-iodotoluene (0.156 ml, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene, then purified by column chromatography (SiO_2, hexane) to provide **5g** as a colorless oil (162 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.85-0.90 (m, 3 H), 1.26-1.32 (m, 4 H), 1.39-1.46 (m, 2 H), 1.61-1.69 (m, 2 H), 2.33 (s, 3 H), 2.82-2.89 (m, 2 H), 7.02-7.06 (m, 1 H), 7.11-7.14 (m, 2 H), 7.18-7.23 (m, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.0, 20.2, 22.5, 28.6, 28.9, 31.4, 32.6, 125.1, 126.2, 127.0, 129.9, 136.4, 136.9. HREI-MS calcd. for $C_{13}H_{20}S$: 208.1285, found: 208.1278.

Hexyl 2,4,6-trimethylphenyl sulfide ***5h*** *(Table 4, entry 8)* Following the general procedure for Table 4, 1-hexanethiol (0.141 mL, 1.0 mmol), 2-iodo-1,3,5-trimethylbenzene (295 mg, 1.2 mmol), **L4** (67.2 mg, 0.2 mmol) in dioxane (1.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **5h** as a colorless oil (142 mg, 60% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 6.8 Hz, 3 H), 1.28-1.44 (m, 6 H), 1.53-1.59 (m, 2 H), 2.30 (s, 3 H), 2.55 (s, 6 H), 2.65 (t, *J* = 7.4 Hz, 2 H), 6.96 (s, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.0, 20.9, 21.9, 22.5, 28.6, 29.9, 31.5, 35.6, 128.8, 130.6, 137.7, 142.8. HREI-MS calcd. for $C_{15}H_{24}S$: 236.1598, found: 236.1605.

Decyl 2,4,6-trimethylphenyl sulfide ***5i*** *(Table 4, entry 9)* Following the general procedure for Table 4, 1-decanethiol (0.220 mL, 1.0 mmol), 2-iodo-1,3,5-trimethylbenzene (295 mg, 1.2 mmol), **L4** (67.2 mg, 0.2 mmol) in dioxane (1.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **5i** as a colorless oil (199 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, *J* = 6.8 Hz, 3 H), 1.30-1.43 (m, 14 H), 1.53-1.60 (m, 2 H), 2.31 (s, 3 H), 2.55 (s, 6 H), 2.65 (t, *J* = 7.4 Hz, 2 H), 6.70 (s, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.1, 20.9, 21.9, 22.7, 29.0, 29.1, 29.2, 29.3, 29.5, 29.9, 31.9, 35.5, 128.8, 130.6, 137.7, 142.8. HREI-MS calcd. for $C_{19}H_{32}S$: 292.2224, found: 292.2216.

Hexyl 4-methoxyphenyl sulfide ***5j*** *(Table 4, entry 10)*[21] Following the general procedure for Table 4, 1-hexanethiol (0.141 mL, 1.0 mmol), 4-iodoanisole (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene (1.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **5j** as a colorless oil (144 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.4 Hz, 3 H), 1.22-1.34 (m, 4 H), 1.36-1.41 (m,

2 H), 1.52-1.60 (m, 2 H), 2.78-2.82 (m, 2 H), 3.77 (s, 3 H), 6.81-6.84 (m, 2 H), 7.30-7.34 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.9, 22.5, 28.3, 29.2, 31.3, 35.7, 55.2, 114.4, 126.9, 132.8, 158.6.

(2-(Benzylthio)phenyl)methanol ***5k*** *(Table 4, entry 11)*[22] Following the general procedure for Table 4, using Cs_2CO_3 (812 mg, 2.5 mmol), benzyl mercaptan (0.118 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), **L3** (36.0 mg, 0.2 mmol) in toluene (1.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **5k** as a colorless oil (147 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (br s, 1 H), 4.03 (s, 2 H), 4.59 (s, 2 H), 7.16-7.24 (m, 7 H), 7.32-7.38 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 39.6, 63.3, 127.2, 127.2, 128.2, 128.2, 128.4, 128.7, 131.5, 133.9, 137.2, 141.6.

Cyclohexyl 4-methylphenyl sulfide ***5l*** *(Table 4, entry 12)*[3c] Following the general procedure for Table 4, using Cyclohexyl mercaptan (0.126 mL, 1.0 mmol), 4-iodotoluene (261 mg, 1.2 mmol), **L4** (67.2 mg, 0.2 mmol) in dioxane (1.0 mL), then purified by column chromatography (SiO_2, hexane) to provide **5l** as a colorless oil (130 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20-1.40 (m, 5 H), 1.57-1.61 (m, 1 H), 1.73-1.77 (m, 2 H), 1.94-1.99 (m, 2 H), 2.32 (s, 3 H), 2.98-3.04 (m, 1 H), 7.09 (d, *J*= 7.6 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.0, 25.7, 26.0, 33.3, 47.0, 129.4, 131.1, 132.7, 136.8.

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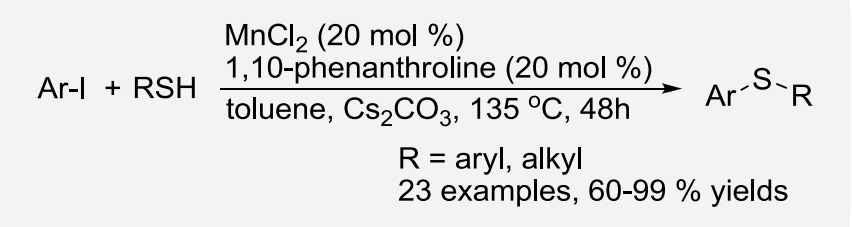

Here we report the manganese-catalyzed coupling reaction of thiols with aryl iodides, giving the aryl thioethers in good to excellent yields. Functional groups such as unprotected alcohol and chloro are tolerated by the reaction conditions. Moreover, this catalytic system enables the sterically demanding aryl iodides to couple with thiols.